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Metal Salts and Surfactant Interaction for Anionic Surfactant Detection: Investigation on Different Types of Surfactant

Tan K Reen[1], Nor Haslina Hashim[1]*

[1]Department of Civil Engineering Technology, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, Hab Pendidikan Tinggi Pagoh, KM 1, Jalan Panchor, 84600 Pagoh, Johor, MALAYSIA.

*Corresponding Author Designation

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Abstract: The common method for anionic surfactant detection is by using methylene blue active substance (MBAS) but this method is tedious and time-consuming due to the repeated extraction with toxic chloroform. Therefore, the purpose of this study is to look into the interaction between the metal salts and surfactant that was proposed and the anionic surfactant without using liquid-liquid extraction. Reagents like Sodium Dodecyl Sulfate (SDS), Copper (II) bromide and Triethylamine (TEA) was prepared and the absorbance was measured using a UV-Vis spectrophotometer after the sample solution of different concentration of SDS, Copper (II) Bromide and TEA were freshly prepared. As a result, Copper (II) Bromide shown good interaction against anionic surfactant (SDS) and a calibration graph of absorbance against concentration with $R^2 = 0.9941$ was plotted. The R^2 value indicates that the value of absorbance is completely explained by the concentration of anionic surfactant. Different types of surfactant like Tween 20 and Triton X-100 (non-ionic) and DDAB (cationic) were also been tested. With the equation y = 0.0812x + 0.05 obtained from the calibration graph, final concentration for all types of surfactant which are Tween 20, Triton X-100 and DDAB including SDS were calculated. It shows that Copper (II) Bromide metal is only had a good response with anionic surfactant (SDS) and shows negative responses to non-ionic surfactant (Tween 20 and Triton X-100) and cationic surfactant (DDAB). This selectivity of surfactant types experiment indicates that the Copper (II) Bromide can be one of the possible metal ions used specifically for anionic surfactant detection and qualification.

Keywords: Anionic Surfactant, Metal Salts, Spectrophotometer, Absorbance

Corresponding author: haslina@uthm.edu.my

1. Introduction

Surfactants are chemicals that lower the surface tension between two liquids or between a liquid and a solid. Any substance that alters the interfacial surface tension is referred to as a surfactant, but in actuality, surfactants can also function as wetting agents, emulsifiers, foaming agents, and dispersants [1]. Pesticides, detergents, petroleum, and cosmetics are among the products that regularly use surfactants in the consumer, industrial, agricultural, and medicinal sectors.

Surfactants are classified into four types. These classifications are based on the polarity of the head group, which can be non-ionic, anionic, cationic, or amphoteric. A non-ionic surfactant has no charge groups in its head. The head of an ionic surfactant has a net charge. The surfactant is referred to as anionic if the charge is negative or cationic if the charge is positive. If a surfactant has a head with two oppositely charged groups, it is said to be zwitterionic [2]. Anionic surfactants (AS) are one of the most common polluted residues in water pollution. According to Grand View Research, anionic surfactants account for 45 percent of the $46 billion worldwide surfactant business.

Anionic surfactants are frequently used in soaps and detergents [3] because they can attack a variety of soils. This is due to the negative charge of the surfactant molecules, which aids in the lifting and suspension of soils in micelles. When anionic surfactants are combined, a large amount of foam is produced. Anionic surfactant in either treated or untreated water could have a negative impact on aquatic life in an environment due to severe alterations in biota that have the ability to bind to bioactive macromolecules and modify their biological activity.

Presence of these pollutants in wastewater is considered as one of the problems, because low biodegradability of these compounds. The discharge of these compounds to the environment can cause foam formation, ground water pollution and create an ecological hazard for aquatic organisms [4]. Anionic surfactant also make many human health problems, including dermatitis and adverse effect on aquatic flora [5].

There have been some attempts in the last 20 years to generalize information on the potentiometric titration of anionic surfactants using ion-selective electrodes (ISEs) and thin-layer chromatography. The most common methods of determining anionic surfactants have been spectrophotometric and potentiometric (using ion-selective electrodes) techniques, including versions of flow injection analysis.

There are many detection and qualification method available but the used of methylene blue active substance (MBAS) is one of the common methods for anionic surfactant analysis using metals. The principle of the determination is that anionic surfactants react with methylene blue in an alkaline medium. This reaction results in salts that are extracted using chloroform. The method was used primarily for determination of anionic surfactants in raw waters according to legislative requirements [6].

However, the method is quite laborious; repeated extraction with toxic chloroform has to be carried out which is also very time-consuming. Meanwhile, there are certain risks when doing the MBAS test as solvent like ethanol, boric acid and Dichloromethane (DCM) were used [7] which can cause hazards. Besides, Methylene Blue (MB) dye is also a hazard to human health above a certain concentration due to its high toxicity. It is toxic, carcinogenic, and non-biodegradable, and it can endanger human health and have a negative impact on the environment. Skin contact with MB may cause redness and itching [8].

Therefore, this study was carried out to investigate the possibility of using the interaction between the proposed metal salts and surfactant without using liquid-liquid extraction as well as to investigate the selectivity of surfactant by constructing a calibration graph. Calibration graph is a standard linear plot of absorbance against concentration, which could be applied to predict the concentration of known absorbance from UV-Vis measurement [9].

Through this investigation, it might potentially detect AS with better properties such as a wider useful concentration range, selectivity, longer lifetime and higher accuracy. If the study is successful, it will undoubtedly make a significant contribution to the scientific community, particularly in the field of surfactant detection in water.

2. Materials and Methods

Figure 1 depicts the methodology flow chart of this study in order to achieve the objectives. The data was obtained using the method depicted in the flow chart.

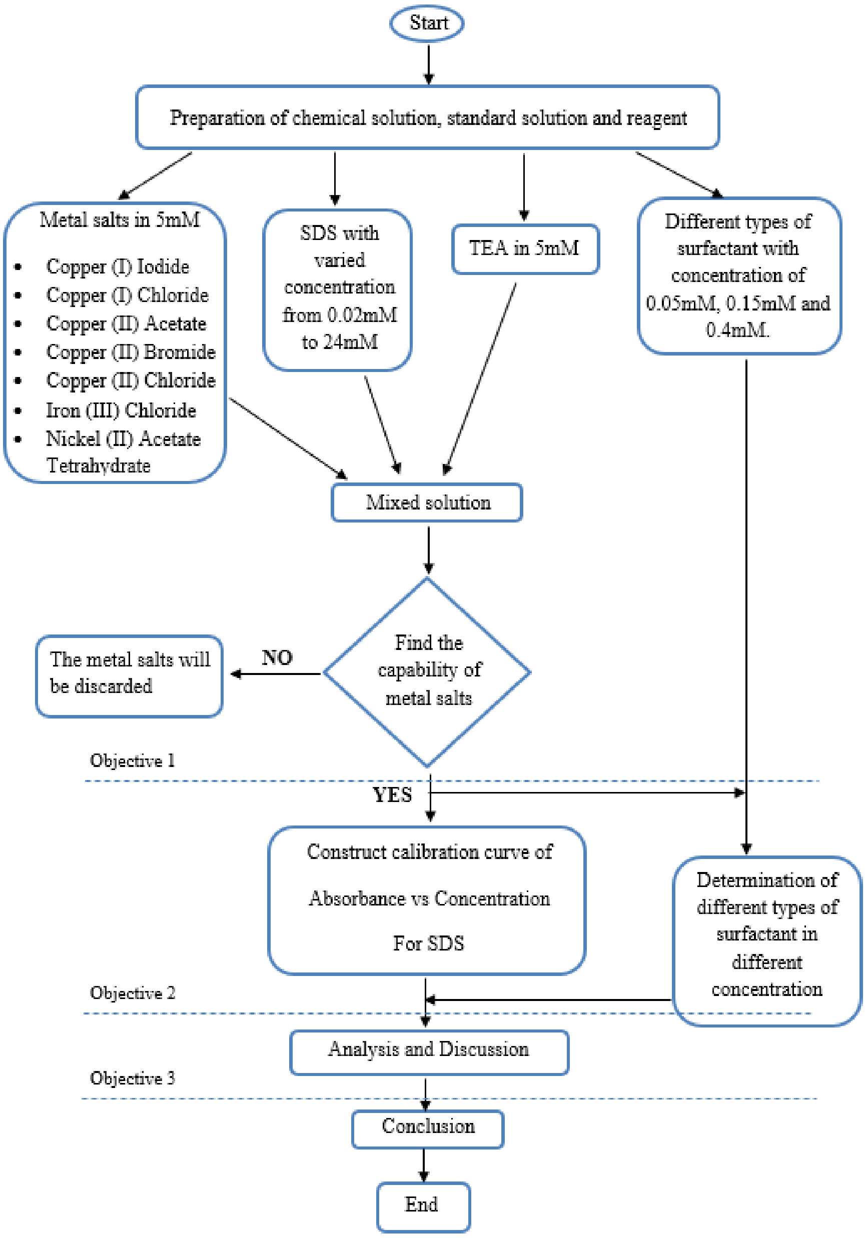

Figure 1: Flow chart of study

2.1 Preparation of metal salts

5mM of stock solution for Copper (II) Bromide, Copper (II) Acetate, Nickel (II) Acetate Tetrahydrate, Copper (I) Chloride, Copper (I) Iodide, Iron (III) Chloride and Copper (II) Chloride were prepared in a 250mL volumetric flask. No. of moles needed was calculated by using Equation 1 with a fixed volume of 250mL and the mass needed was calculated by using Equation 2.

2.2 Preparation of SDS in different concentration

24mM of stock solution for SDS was prepared in a 1L volumetric flask. Next was by using Equation 3 to dilute the 24mM stock solution to 0.1mM, 0.5mM, 1mM, 3mM, 5mM, 7mM, 8mM, 9mM and 10mM in a 100mL volumetric flask respectively using a volumetric pipette.

2.3 Preparation of Triethylamine, TEA

5mM of stock solution for TEA was prepared in a 250mL volumetric flask using micropipette in a fume hood. The molarity of TEA was calculated by using Equation 4 then the volume needed was calculated with a fixed volume of 250mL by using Equation 3.

2.4 Preparation of different types of surfactant

0.4mM of stock solution for Tween 20, Triton X-100 and DDAB were prepared in a 250mL volumetric flask using micropipette. The molarity of Tween 20 and Triton X-100 was calculated by using Equation 4 then the volume needed was calculated with a fixed volume of 250mL by using Equation 3 while the no. of moles needed for DDAB was calculated by using Equation 1 with a fixed volume of 250mL and the mass needed was calculated by using Equation 2. Next, Tween 20, Triton X-100 and DDAB each were diluted into 0.05mM and 0.15mM in a 100mL volumetric flask respectively from the 0.4mM stock solution using the Equation 3.

2.3 Methods

The spectrophotometric method for the determination of anionic surfactant without liquid-liquid extraction was adopted in this study. Spectrophotometric determination of anionic surfactants was carried out with wavelength from 400nm to 800nm with the use of a UV-Vis spectrophotometer. Firstly, mixed solution of metal salts, SDS and TEA was prepared and tested. Then, one metal salt was chosen which was Copper (II) Bromide and was mixed well with different concentration of SDS (0.04mM, 0.05mM, 0.06mM, 0.1mM, 0.15mM, 0.2mM and 0.5mM). There were total of seven samples and TEA was added to each of them. Absorbance was recorded and measured between wavelength 400nm to 800nm using spectrophotometer. Then, a calibration graph of Absorbance against Concentration was plotted with a constant wavelength. After that, SDS was changed to different type of surfactants which are non-ionic surfactant, Tween 20 and Triton X-100; cationic surfactant, Didodecyldimethylammonium Bromide (DDAB) to observe the interaction between Copper (II) Bromide. Copper (II) Bromide was mixed well with different concentration of Tween 20 (0.05mM, 0.15mM and 0.4mM) followed by TEA. This step was repeated for Triton X-100 and DDAB as well. Absorbance was measured between wavelength 400nm to 800 nm using spectrophotometer. A graph of Absorbance against Wavelength was plotted where the absorbance value (y) can be obtained to calculate the final concentration based on the calibration graph (x) for each type of surfactants tested in this study.

2.3 Equations

Equation to calculate the no. of moles,

$$M = \frac{n}{v} \qquad Eq. 1$$

Where M is the molarity (M), n is the no. of moles and v is the volume (mL).

Equation to calculate the mass needed,

$$Moles = \frac{Mass}{MW} \qquad Eq. 2$$

Where MW is the molecular weight (g/mol).

Equation to calculate volume for dilution,

$$m_1 v_1 = m_2 v_2 \qquad Eq. 3$$

Where m_1 is the initial concentration (mM), v_1 is the initial volume (mL), m_2 is the final concentration (mM) and v_2 is the final volume (mL).

Equation to calculate the molarity,

$$M = \rho \times \frac{1}{MW} \qquad Eq. 4$$

Where M is the molarity (M), ρ is the density and MW is the molecular weight.

3. Results and Discussion

3.1 Determination of metal salts

The graph of absorbance against wavelength was plotted as shown in Figure 2 as a comparison of metal salts stability.

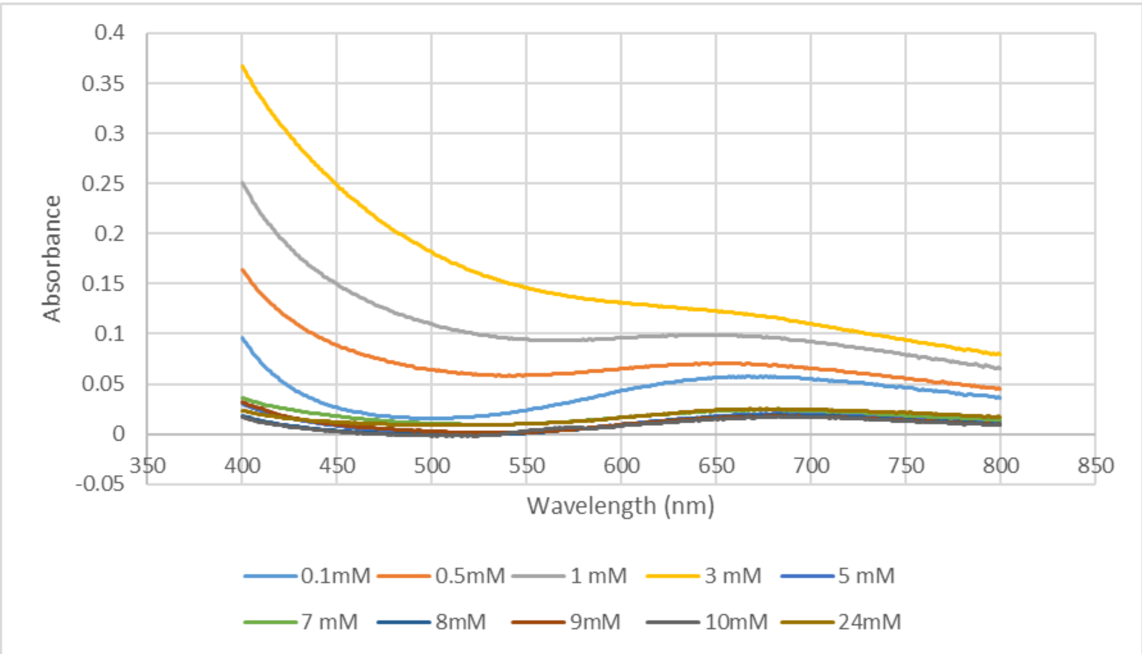

Figure 2: Graph of Absorbance against Wavelength for Copper (II) Bromide

The metal salts, Copper (II) Bromide, exhibited the most stable graph interaction with SDS. Based on the graph shown above, this is because it shows a trend, has the least fluctuation, and overlaps. It also shows a smooth curve with no intersection for concentrations of 0.1mM, 0.5mM, 1mM, and 3mM. Furthermore, it increases significantly at 650nm.

As a result, Copper (II) Bromide was chosen, and the concentration range of 0.04mM to 0.5mM was determined using this result. Copper (II) Bromide complexes behaved similarly to surfactant (SDS) because of their mononuclear nature and shared structural characteristics. It showed an increase in absorption with the addition of surfactant solution [10]. Thus, Copper (II) Bromide was suitable for the anionic surfactant detection in this study.

3.2 Interaction of anionic surfactant (SDS) with Copper (II) Bromide

The absorbance was recorded at a wavelength range of 400nm to 800nm using the UV-Vis spectrophotometer. Graph of Absorbance against Wavelength was plotted shown in Figure 3.

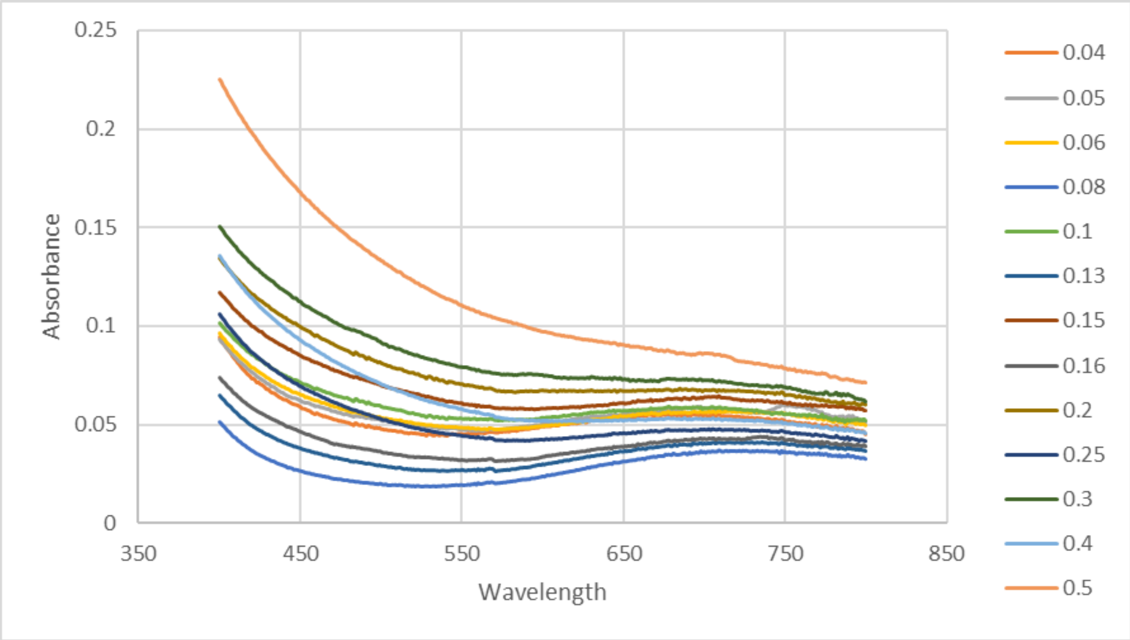

Figure 3: Graph of Absorbance against Wavelength for Copper (II) Bromide

There is a head electrostatic interaction between positive charge of triethylamine, TEA and negative SDS. The surfactant–metal complex where a coordination complex which containing a central metal ion surrounded by ligands coordinated to the metal. In these surfactants, the entity containing the central metal ion, along with its primary coordination sphere, acts as the head group and hydrophobic entity of one or more of the ligands acts as the tail part. Thus, the data was analyzed as shown in Table 1 and a calibration graph, Absorbance against Concentration of SDS for Copper (II) Bromide with wavelength 650nm was plotted shown in Figure 4.

Table 1: Data analysis for Copper (II) Bromide

Concentration (mM)	Absorbance
0.04	0.05378443
0.05	0.05560023
0.06	0.0541702
0.10	0.05706684
0.15	0.06114322
0.20	0.06712156
0.50	0.09077856

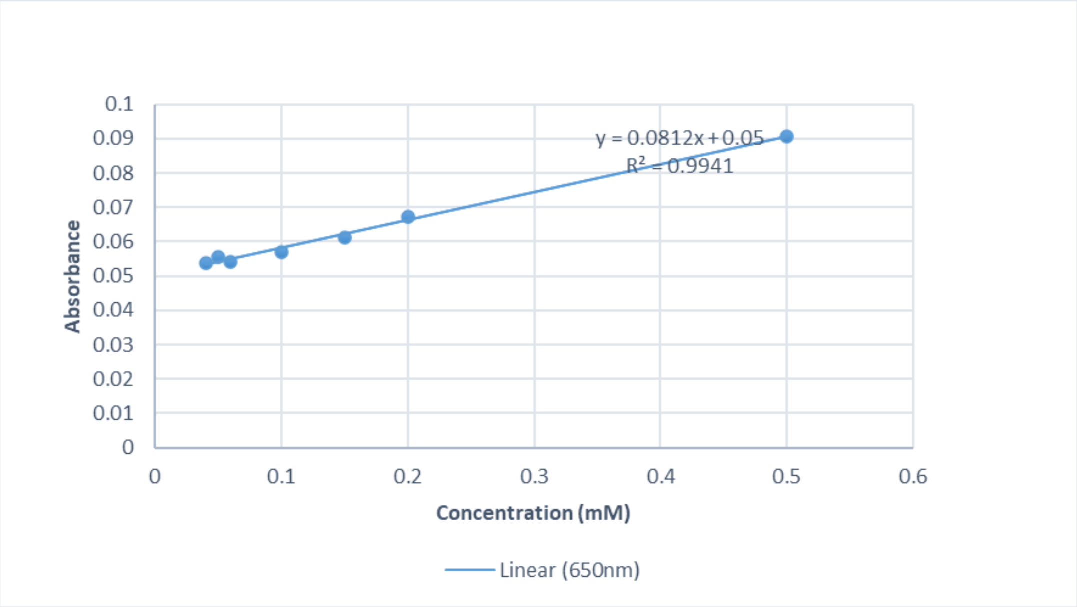

Figure 4: Absorbance against Concentration of SDS for Copper (II) Bromide

Calibration curve was constructed as it is a standard linear plot of absorbance against concentration, which could be applied to predict the concentration of known absorbance from UV-Vis measurement [9] by using the equation, $y = 0.0812x + 0.05$ shown in Figure 4.

3.3 Response of different types of surfactant on the Copper (II) Bromide to anionic surfactant

The final concentration based on the calibration graph, x (mM) were calculated and tabulated in Table 2.

Table 2: Final concentration based on the calibration graph for each types of surfactant

Prepared Concentration (mM)	Types of Surfactant		Absorbance, y	Final Concentration, x (mM)
0.05	**Anionic**	**SDS**	0.054	**0.049**
	Non-ionic	**Tween 20**	-0.008	**-0.714**
	Non-ionic	**Triton X-100**	-0.010	**-0.739**
	Cationic	**DDAB**	0.018	**-0.394**
0.15	**Anionic**	**SDS**	0.062	**0.148**
	Non-ionic	**Tween 20**	0.017	**-0.406**
	Non-ionic	**Triton X-100**	0.010	**-0.493**
	Cationic	**DDAB**	-0.007	**-0.702**
0.4	**Anionic**	**SDS**	0.052	**0.025**
	Non-ionic	**Tween 20**	-0.006	**-0.690**
	Non-ionic	**Triton X-100**	-0.004	**-0.665**
	Cationic	**DDAB**	0.017	**-0.406**

Results obtained in Table 2 shows good indicator in terms of qualitative and quantitative determination. It is when researchers collect a water sample with unknown surfactant and undergo UV-Vis spectrophotometer testing, if the reading shown is negative then it indicates that the SDS does not exist in the water sample. If the reading shown is positive then it implies that the SDS does exist in the water sample. This may also imply that the metal salts were not having a good interaction with non-ionic surfactant (Tween 20 and Triton X-100) and cationic surfactant (DDAB) although they are also surfactant.

The ion pairing mechanism of Tween 20, Triton X-100 and DDAB with Copper (II) Bromide which carried a positive charge does not formed well as Tween 20 and Triton X-100 carried no charge while DDAB carried a positive charge. This is because electrostatic attractive forces between the cation and anion hold an ion pair together.

It is crucial to obtain the selectivity towards anionic surfactant as it is the most common and commonly used surfactants, appearing in practically every cleaning product. It can produce large amount of foam compared to others. It can enter the aquatic environment through wastewater treatment plants (WWTPs) discharge into rivers, oceans, lakes, and estuaries, or through direct discharge of raw sewage. Therefore, the amounts of surfactants and their degradation products in environmental matrices should be determined because of the threats they pose to the environment. Surfactant detection in the lab, on the other hand, could be a challenging task to complete.

4. Conclusion

The study revealed that the Copper (II) Bromide has good interaction with anionic surfactant, SDS and a 99% calibration graph with $R^2 = 0.9941$ was constructed. The result shows that the final concentration for anionic surfactant shows positive reading while the others show negative reading. Although non-ionic surfactant which are Tween 20 and Triton X-100; and cationic surfactant, DDAB are also surfactants but they are not interacting well with metal salts in this study. It implies that this study is specific and selective only to anionic surfactant detection. This selectivity of surfactant types experiment indicates that the Copper (II) Bromide can be one of the possible metal ions used specifically for anionic surfactant detection and qualification only. This study showed that Copper (II) Bromide has a new capability for detecting anionic surfactants. It is expected that anionic surfactant detection in water samples can be detected not only qualitatively but also quantitatively.

However, a detailed and full investigation of metal salts-surfactant response of other surfactant is still required to ensure the selectivity of anionic surfactant by metal salts is genuine. More investigations are needed in surfactant detection, such as sample's replication for statistical confirmation study, used other types of anionic, cationic, and non-ionic surfactants, such as Linear Alkylbenzene Sulfonates (LAS), Quaternary Ammonium Compounds (QAC), and Alkylphenol ethoxylate (APE), and their interactions in a mixed solution and also in a real environmental water sample.

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